



Aerobic Oxidation of HMF to FDA with Ruthenium containing Ferrite-Spinel Catalyst

Eyjolfsdottir, Ester; Riisager, Anders

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Ester Eyjólfssdóttir, Anders Riisager

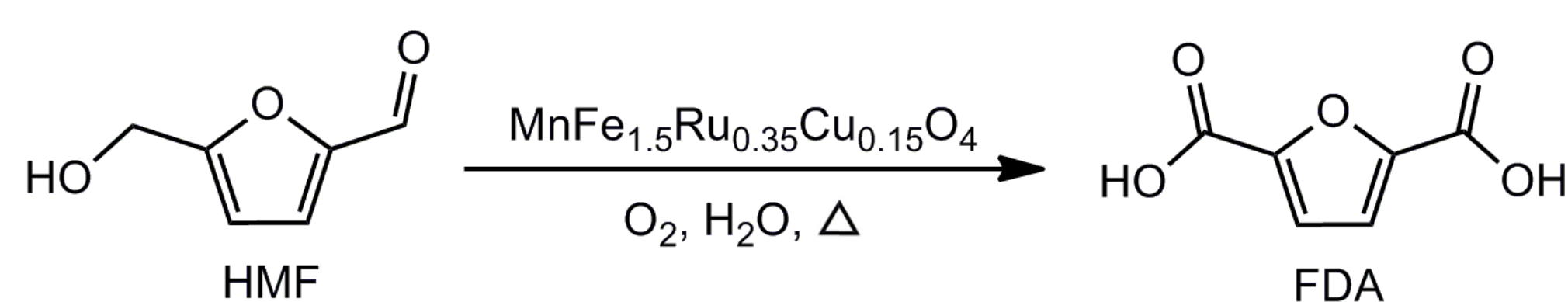
Centre for Catalysis and Sustainable Chemistry (CSC),
Department of Chemistry, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

eieyj@kemi.dtu.dk

Introduction

In the past years, there has been a rising demand for efficient heterogeneously catalyzed oxidation processes for production of both fine and bulk chemicals [1]. In order to avoid waste generation, considerable effort has been put into the development of aerobic oxidation methods using molecular oxygen as the stoichiometric reagent. Recent studies have shown that ruthenium oxides are active oxidation catalysts for various functional groups [2].

In this work we have used a ferrite-spinel based catalyst, $\text{MnFe}_{1.5}\text{Ru}_{0.35}\text{Cu}_{0.15}\text{O}_4$, previously described by Ji et al. [3] to efficiently oxidize 5-hydroxymethyl furfural (HMF) to 2,5-furandicarboxylic acid (FDA) in water in the presence of molecular oxygen:



Why HMF and FDA?

- HMF can be obtained from biomass via dehydration of hexose monosaccharides, such as glucose or fructose [4], and is a precursor for many compounds with high industrial potentials, such as FDA, figure 1.
- FDA has been identified as an important value added chemical by the U.S. Department of Energy biomass program [5].
- FDA can replace chemicals derived from fossil fuels in manufacture of polyamides, polyesters, and polyurethanes.

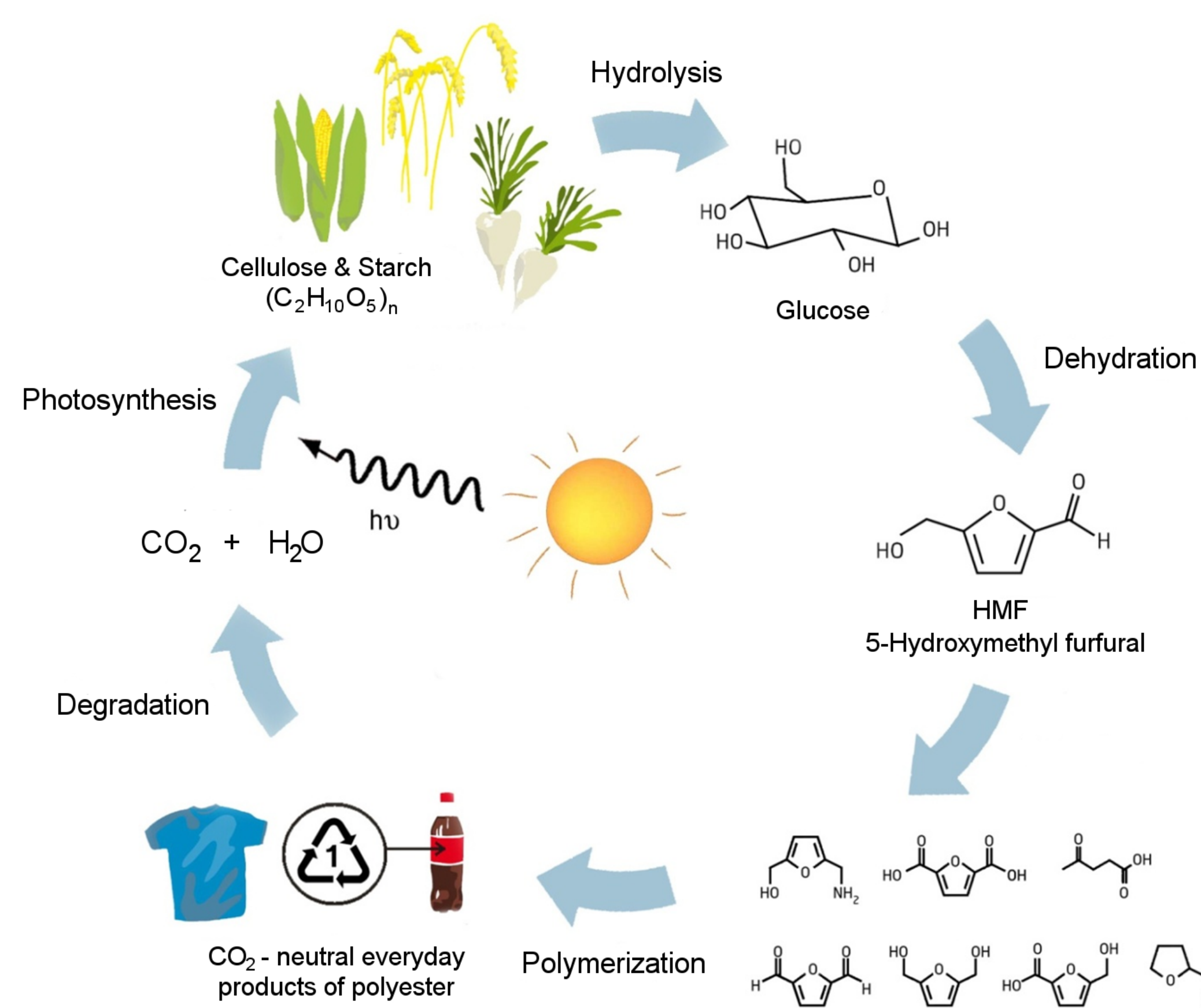


Figure 1: Reaction network and lifecycle of HMF as a renewable platform molecule.

Reaction pathway

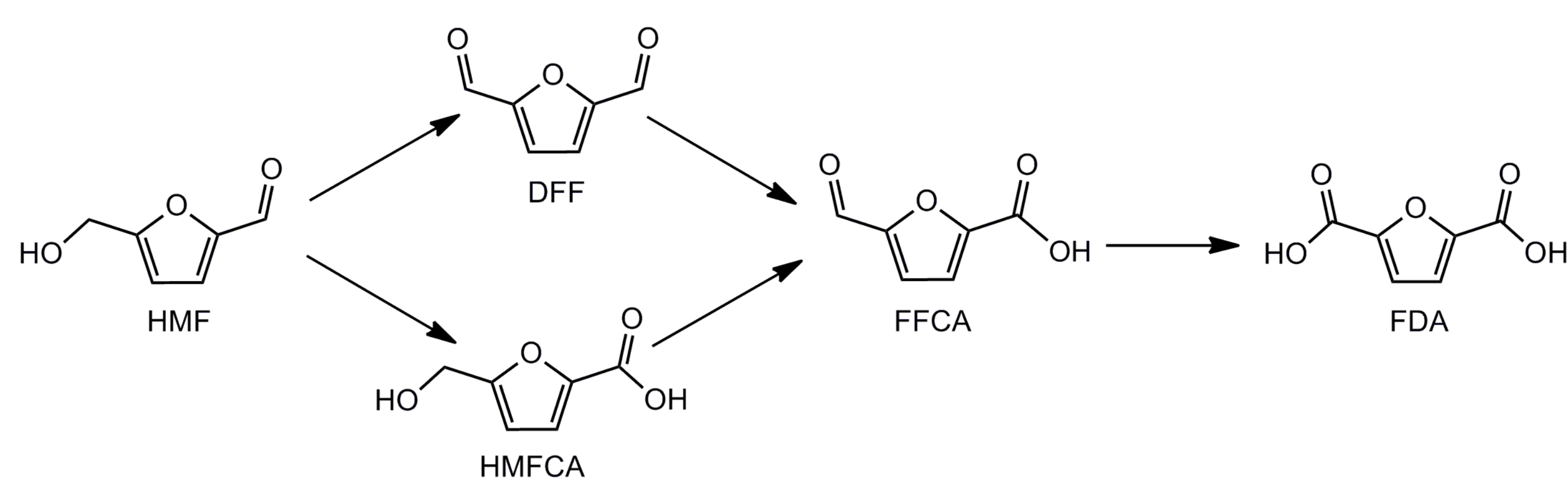


Figure 2: Possible reaction pathways for the oxidation of HMF to FDA.

The oxidation of HMF to FDA can proceed via two pathways; oxidation of the alcohol group to aldehyde, forming diformyl furan (DFF) or oxidation of the aldehyde group to carboxylic acid, forming 5-hydroxy-2-furancarboxylic acid (HMFCFA). Further oxidation of both DFF and HMFCFA yields 5-formylfuran-2-carboxylic acid (FFCA) and then, FDA.

Experimental and Results

The catalyst, $\text{MnFe}_{1.5}\text{Ru}_{0.35}\text{Cu}_{0.15}\text{O}_4$ was prepared as described by Ji et al. [3]. All reactions were carried out in a stirred Parr reactor autoclave, and the degree of conversion and yields of individual products were quantified by HPLC.

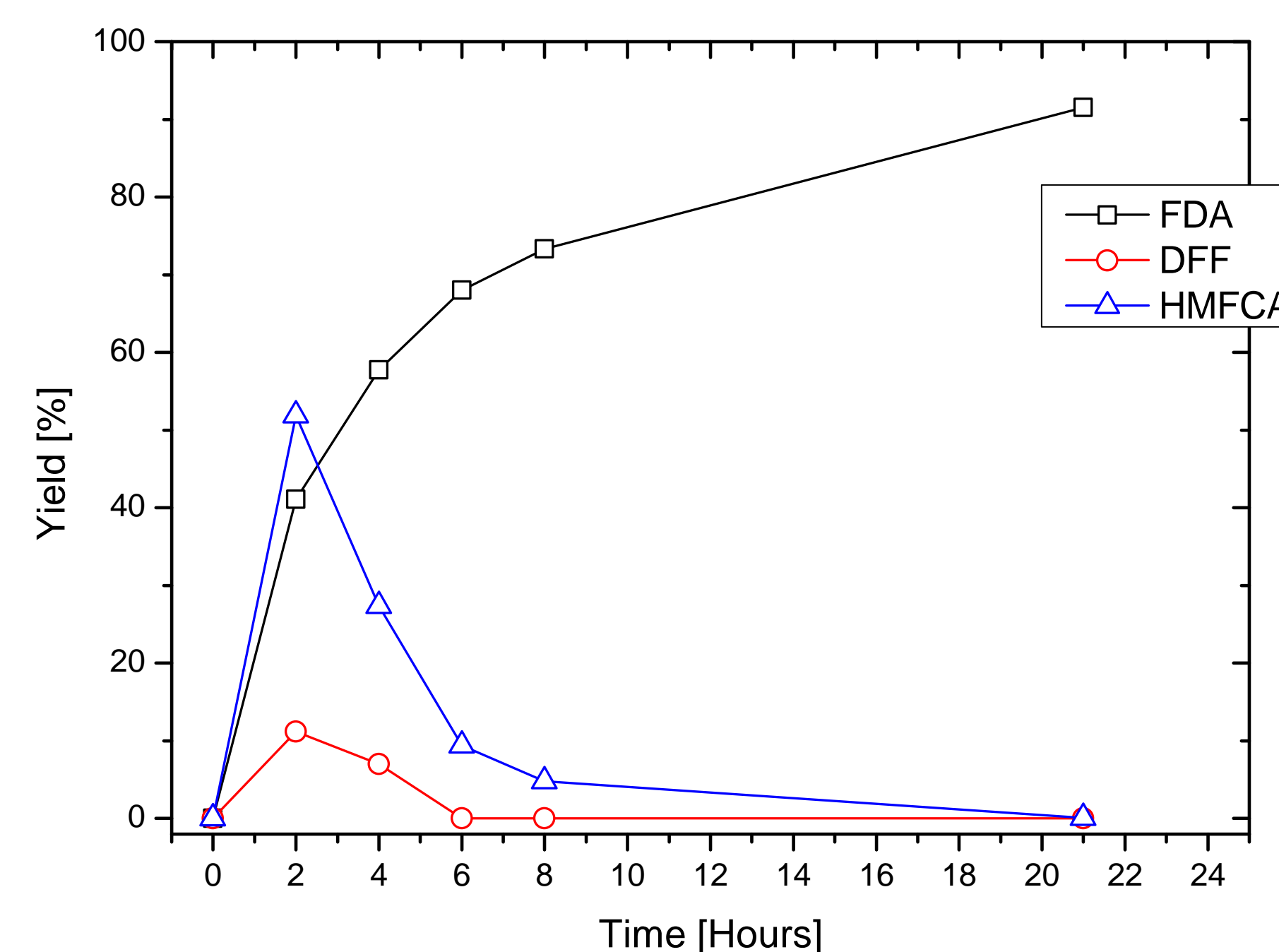


Figure 3: Product yields as a function of reaction time. Reaction conditions: 10 mL 2.2 wt% HMF in aqueous solution, molar ratio of catalyst to HMF = 0.55, 10 bar O_2 , 110°C. Full conversion of HMF was achieved in all reactions.

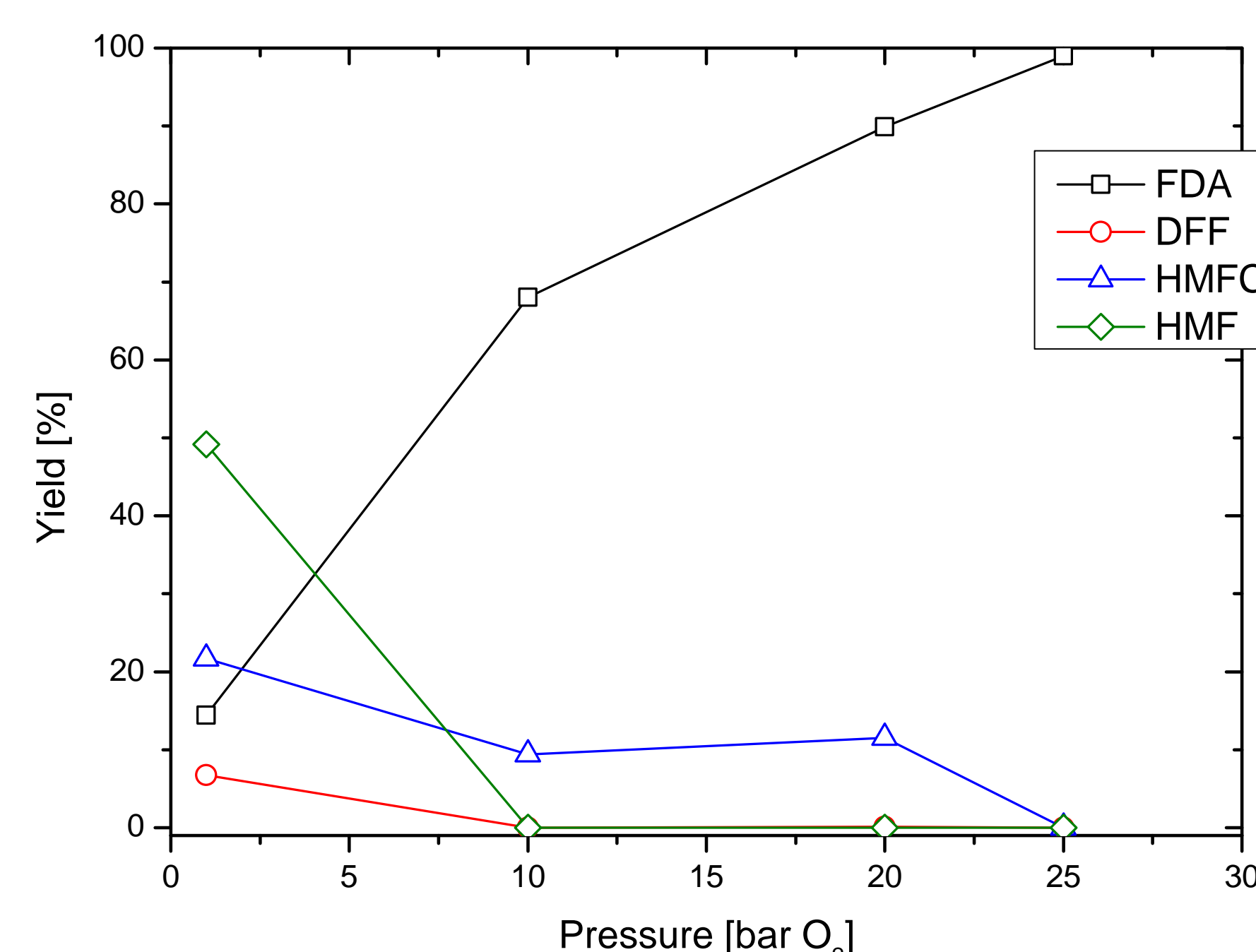


Figure 4: Product and HMF yields as a function of oxygen pressure. Reaction conditions: 10 mL 2.2 wt% HMF in aqueous solution, molar ratio of catalyst to HMF = 0.55, 110°C, 6 hours.

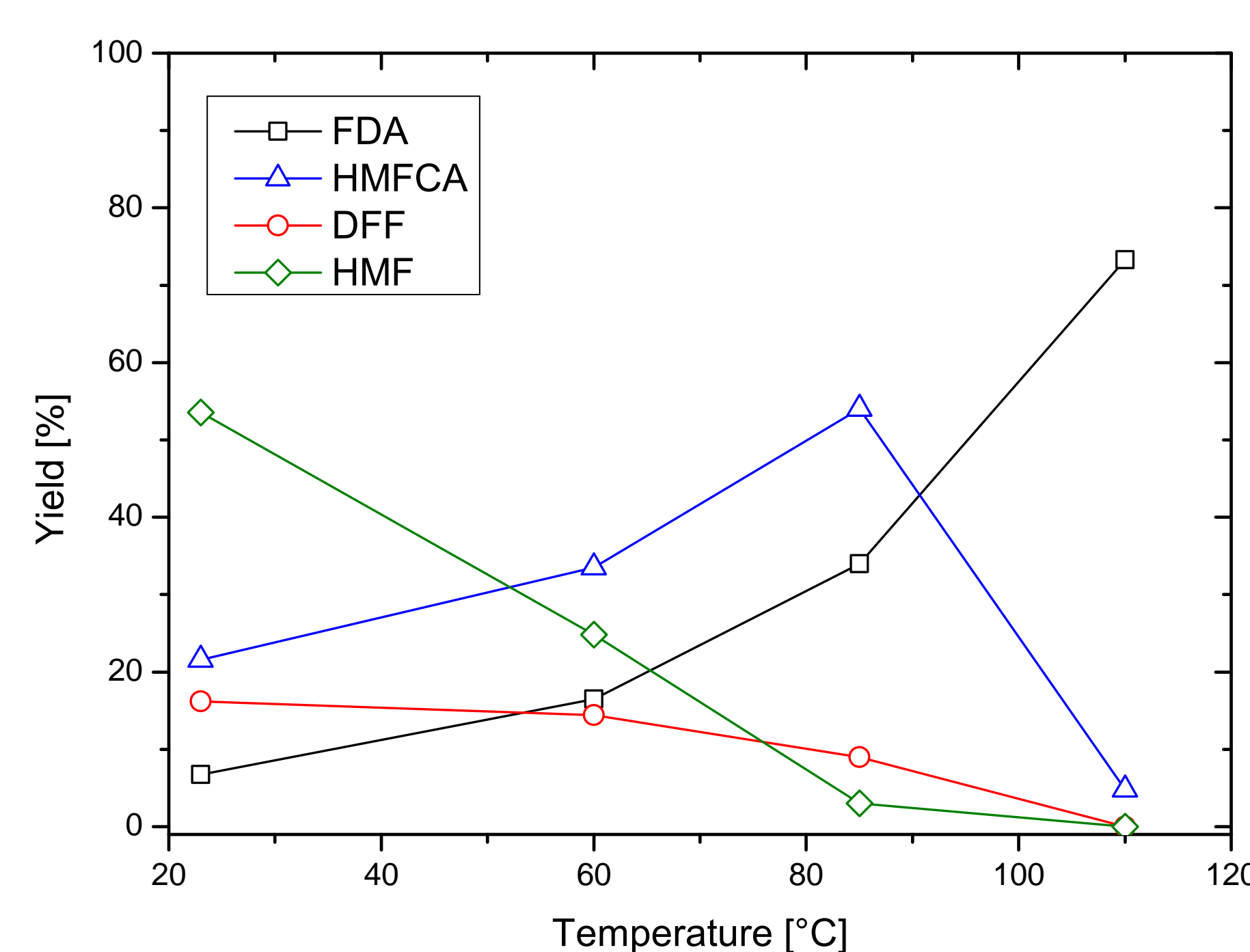


Figure 5: Product and HMF yields as a function of reaction temperature. Reaction conditions: 10 mL 2.2 wt% HMF in aqueous solution, molar ratio of catalyst to HMF = 0.55, 10 bar O_2 , 6 hours.

Conclusions

- Quantitative yields of FDA can be achieved at 110°C and 25 bar O_2 in 6 hours using 2.2 wt% aqueous solution of HMF and molar ratio of Ru to HMF of 0.19.
- Increased oxygen pressures and increased reaction temperatures have positive effect on the reaction rate, although too high temperatures have been shown to cause degradation of HMF.
- Detection of both DFF and HMFCFA in post-reaction mixtures suggests that the reaction proceeds via both possible reaction pathways shown in figure 2.

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